Ultra-selective epoxidation of styrene on pure Cu{111} and the effects of Cs promotion

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Styrene undergoes efficient epoxidation to styrene epoxide on the Cu{111} surface. At the optimum condition ($\Theta_O = 0.03$ ML) ∼20% of the styrene is converted to the epoxide with almost 100% selectivity. Comparison with Ag{111} shows that the epoxidation activity and selectivity of Cu greatly exceed those of Ag. Incipient oxidation of the Cu{111} surface does not suppress the adsorption of styrene, but the oxidised metal is catalytically inert. Submonolayer amounts of Cs enhance styrene uptake and increase conversion to the epoxide without adversely affecting epoxidation selectivity. This effect is due to inhibition of Cu oxidation by Cs. Our findings are discussed in the light of current understanding of Ag-catalysed alkene epoxidation.

Keywords: epoxidation, styrene, Cu{111}-catalysed, Cs, promotion

1. Introduction

There have been many studies of the Ag-catalysed partial oxidation of ethene to the epoxide. This reflects the intrinsic interest attached to this apparently unique process and also its major industrial importance [1]. Ethene epoxide is manufactured on a very large scale: it is a strategically important intermediate in modern chemical technology. The reaction mechanism has been studied using both dispersed catalysts and single crystal model systems, the latter yielding clear evidence about the nature of the active oxygen species and mode of promoter action [1,2]. The single crystal data show that although both atomic and molecular forms of adsorbed oxygen are present on Ag, it is the oxygen adatoms that are responsible for all catalytic activity: adsorbed dioxygen is merely a spectator. These findings contradict the understandably attractive hypothesis made popular by Sachtler and his co-workers [3], namely that O_2(a) is responsible for epoxidation and O(a) for ethene burning. The Sachtler hypothesis appeared to account in a natural way for the apparently unique epoxidation activity of Ag – that is, only Ag adsorbs dioxygen. However, if dioxygen on silver is just a spectator, why should other metals not catalyse alkene epoxidation? In attempting to answer this question, one should not overlook the chemisorption mode of the alkene, which must also be an important issue. Both the oxygen and the alkene need to be adsorbed in the appropriate chemical state. On Ag, ethene adsorbs with minimal rehybridisation of the olefinic π bond. Oxygen insertion to yield the epoxide is therefore possible. In contrast, on Ni and Pt surfaces, for example, the alkene is present as a di-σ-bonded species: the possibility of epoxidation is eliminated, whatever the state of the adsorbed oxygen.

Alkene adsorption on Cu resembles alkene adsorption on Ag – a π-adsorbed molecule is formed [4]. Moreover, under appropriate conditions, O adatoms can be generated on Cu surfaces [5]. Therefore, if our view of the reaction mechanism is essentially correct, it should be possible to expoxidise terminal alkenes on Cu surfaces.

Very recently, we demonstrated that Cu-catalysed alkene epoxidation is indeed possible. In particular, we showed that styrene adsorbed on Cu{110} undergoes extremely efficient epoxidation [6]. The adsorption geometry of the alkene was determined by NEXAFS and major changes in the activity of the Cu surface as a function of oxygen coverage were demonstrated. The wider implications of this discovery are as follows. We have shown that on Ag{111} [7] and Ag{100} [8] the epoxidation behaviour of styrene under UHV conditions, *and* its response to chlorine and alkali promoters, closely mimics that of ethene itself. That is, styrene is a useful model alkene for use in mechanistic investigations of terminal alkene epoxidation. The higher adsorption enthalpy of styrene compared to ethene is a major asset in studies carried out under ultrahigh vacuum conditions: in temperature-programmed experiments it reacts before significant desorption occurs.

Here we report on styrene epoxidation catalysed by the Cu{111} surface whose oxygen adsorption properties differ from those of the Cu{110} surface. We also examine the effect of co-adsorbed Cs: recall that alkalis are important selectivity promoters for Ag epoxidation catalysts [9]. Significant differences are found between these two Cu surfaces, particularly in regard to reaction kinetics. This implies that particle size effects could be significant in epoxidation with dispersed Cu catalysts. We also show that the

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effect of Cs on Cu-catalysed epoxidation is very different from the effect of alkalis in Ag-catalysed epoxidation. Our results are discussed in the light of current understanding of Ag-catalysed epoxidation in an attempt to arrive at a coherent view of the behaviour of Cu and Ag as epoxidation catalysts.

2. Experimental

Experiments were performed in a UHV chamber operated at a base pressure of 1×10^{-10} Torr [10]. The Cu{111} crystal could be resistively heated to 850 K and cooled to 160 K. Cleaning was achieved by cycles of Ar^+ sputtering (1 kV, 4 μA) followed by annealing at 800 K for 10 min until no impurities were detectable by XPS. XP spectra were obtained with Al K_α radiation using a VSW HA100 hemispherical analyser and single-channel detector. Multiplexed TPR spectra were acquired at a constant heating rate of 5 $K\,s^{-1}$ by means of a VG SensorLab quadrupole mass spectrometer. The signals at $m/z = 2$, 18, 28, 44, 78, 91, 104 and 120 were monitored simultaneously. $m/z = 91$ and 104 are the principal ion fragment peaks for styrene epoxide and styrene, respectively; they provide unambiguous fingerprints for the desorption of these species. Cs dosing was achieved by vacuum evaporation of the metal from a SAES getter filament. Coverages of Cs were calculated by means of the intensity ratio of the Cs(3d) and Cu(2p) emission (I_{Cs}/I_{Cu}). At room temperature Cs adsorption results in a Cu{111}-p(2 × 2)-Cs reconstructed surface [11,12]. This corresponds to saturation coverage and is equivalent to 0.25 monolayers (ML) of Cs. O_2 exposures were performed by backfilling the chamber to the desired pressure, and styrene doses were delivered using a 6 mm diameter collimator tube. Oxygen coverages were estimated by means of the intensity ratio of the O(1s) and Cu(2p) emission (I_O/I_{Cu}). It is known that at room temperature saturation with oxygen results in a complex reconstructed Cu_2O-like surface which corresponds to $\Theta_O = 0.5$ ML [12]. Gas exposures are quoted in langmuirs ($1\ L = 1\times10^{-6}$ Torr s); they are accurate in the case of the O_2 exposures but correspond to an upper limit in the case of styrene doses, no correction having been applied for the higher ionisation gauge sensitivity.

3. Results and discussion

At 170 K styrene chemisorbs on Cu{111} without dissociation, and subsequent thermal desorption spectra exhibit two partially resolved maxima at 250 and 400 K (figure 1(a), spectrum 1). These maxima are apparent at all coverages; that is, the associated adsorption states do not fill sequentially but simultaneously. This is distinctly different from the behaviour of styrene on Cu{110} where only the 400 K maximum is observed [6]. Recall that the adsorption geometry of styrene on Cu{110} has been determined [6]: NEXAFS data show that only a single type

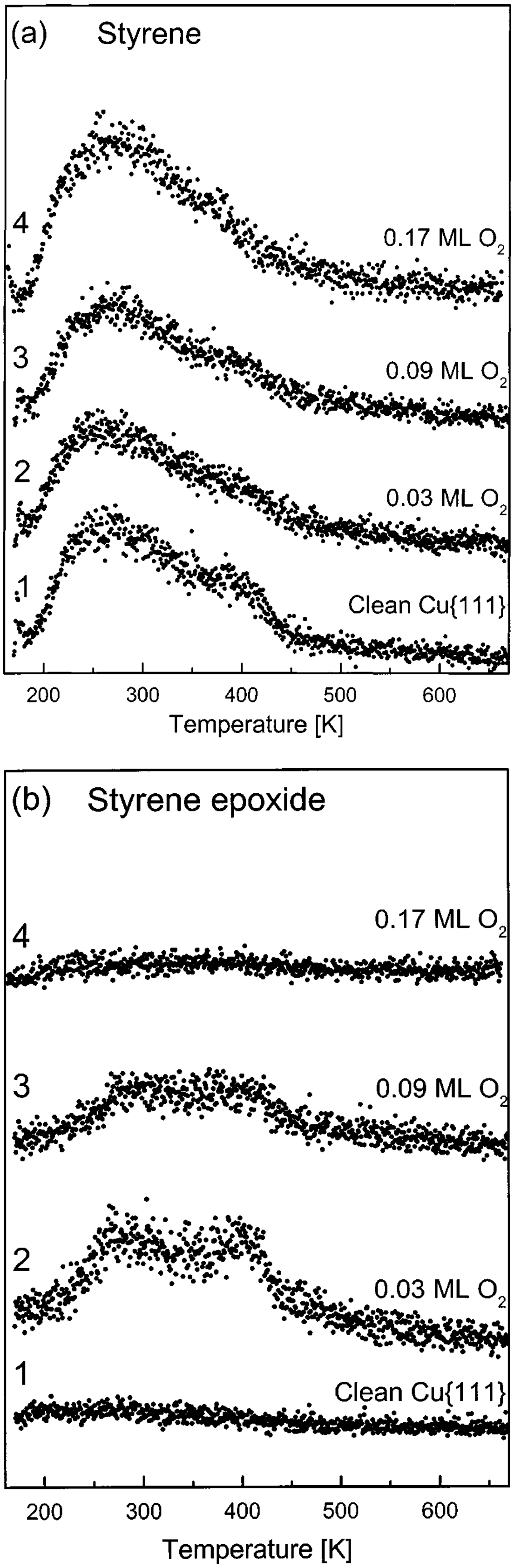

Figure 1. TPR spectra for (a) styrene ($m/z = 104$) and (b) styrene epoxide ($m/z = 91$) from (1) clean Cu{111}, and from oxygen predosed Cu{111} surfaces with oxygen coverages of (2) 0.03, (3) 0.09 and (4) 0.17 ML.

of chemisorbed styrene is formed. In the present case, deliberate Ar^+ sputtering of the clean surface before styrene adsorption increased the population of the higher temperature state, suggesting that it corresponds to adsorption at defect sites.

Temperature-programmed reaction after oxygen preadsorption at 170 K, followed by a saturation dose of styrene (1 L) at 170 K, results in formation of styrene epoxide. Representative data are shown in figure 1(b): the corresponding desorption spectra of unreacted styrene, acquired simultaneously, are presented in figure 1(a) (spectra 2, 3 and 4). No CO_2 or H_2O were detected under any conditions, indicating very efficient epoxidation with selectivity approaching 100%.

An oxygen pre-dose of 0.5 L ($\Theta_O \approx 0.03$ ML) resulted in the highest yield of epoxide: increased oxygen pre-coverage *decreased* conversion, eventually suppressing all reactivity at $\Theta_O \approx 0.17$ ML. Notice that the total uptake of styrene is relatively unaffected by the amount of pre-adsorbed oxygen, so the quenching of activity at higher oxygen coverages is not associated with inhibition of styrene adsorption. There is also no oxidation activity at saturation oxygen pre-coverage ($\Theta_O \approx 0.5$ ML) which corresponds to completion of a Cu_2O-like surface phase [14].

The reactively formed styrene oxide desorbs with rate maxima at ~280 and ~400 K suggesting that one is dealing with two different rate processes associated with two different states of adsorbed styrene. This possibility is strengthened by the observation that on Cu{110} there is only one form of adsorbed styrene and that this is associated with just a single styrene oxide rate maximum at ~400 K [6]. In this sense we may conclude that the {111} surface exhibits potential for higher catalytic activity than the {110} plane since the former provides an additional low-temperature reaction pathway. These differences between the two copper surfaces imply that particle size effects are likely to be significant in epoxidation catalysis by dispersed Cu catalysts.

Note that the desorption temperature of styrene, particularly with reference to the ~400 K process, decreases with increasing oxygen pre-coverage (figure 1(a)). A similar effect, though much more pronounced, was also observed on Cu{110} [6]. In that case the weaker adsorption could be interpreted with confidence in terms of styrene adsorption on growing islands of the Cu{110}-p(2 × 1)-O structure which represents the first stages of copper oxide growth. Nucleation and growth of the metal oxide would also account for changes in reactivity of the oxygen: that is, the chemistry of oxygen adatoms *versus* oxidic oxygen.

Our data suggest that similar factors are at work in the present case as well. Thus the minimum necessary and sufficient conditions for styrene epoxidation on Cu{111} appear to be oxygen adatoms and styrene molecules adsorbed on Cu metal sites in the vicinity of these oxygen adatoms. Again, the implication is that the chemical state of oxygen is critically important, oxidic oxygen being an ineffective electrophile with respect to the adsorbed alkene. In this regard the epoxidation chemistry parallels that observed on Ag where the valence charge density on oxygen determines selectivity [15]. On Ag, the charge density on oxygen can be diminished by co-adsorbed Cl, thus creating a better electrophile and favouring epoxidation. Alkalis have the opposite effect, favouring combustion over epoxidation [7]. Cu, unlike Ag, readily forms the metal oxide, even under UHV conditions. If, as seems likely, the transition from chemisorbed oxygen to Cu oxidation is accompanied by a significant change in the valence charge density on oxygen, the present results may be explained on similar basis to that used in the case of Ag [15]. Chemisorbed oxygen on Cu is a good electrophile for the π-adsorbed alkene. Oxidic oxygen (formally O^{2-}) is a poor electrophile and, therefore, ineffective for epoxidation.

We also investigated the effects of adding varying amounts of Cs on the adsorption and reactivity of styrene on Cu{111} oxygenated to the optimum degree. That is, the oxygen coverage corresponding to maximum activity ($\Theta_O \approx 0.03$ ML). The clean Cu surface was first dosed with different amounts of Cs, followed by a constant oxygen dose of 0.5 L and a (saturating) styrene dose of 1 L. The results are illustrated in figure 2 (a) and (b). (For oxygen pre-coverages higher than 0.03 ML, the conversion decreased progressively, being fully quenched at 0.17 ML O_2, just as in the case of the alkali-free surface.)

It is clear that the presence of Cs sharpens and downshifts the styrene desorption spectrum to lower temperatures (cf. spectra 1, 2 and 3 in figure 2(a)) presumably due to the effects of CsO_x (see below) on the chemisorption of styrene. It is also apparent that at 0.07 and 0.15 ML Cs there is an increase of ~30% in styrene uptake relative to the clean Cu surface. These effects are accompanied by a lowering in temperature for styrene oxide production (~240 K) and a ~30% increase in the styrene oxide yield (cf. figure 2(b), spectra 1 and 2).

Spectra 4 in figure 2 (a) and (b) were obtained after adsorbing styrene on a relatively thick film of Cs oxide. This Cs oxide film (estimated thickness was 10–12 ML) was prepared by repeated cycles of Cs deposition followed by oxidation at room temperature, until no signature of the Cu substrate was detectable by XPS. It consisted of Cs_2O and Cs_2O_2 detected by their characteristic O(1s) binding energies of 530.8 and 533.3 eV [16]. The data show that these oxides of Cs are inactive towards styrene and therefore not directly involved in the epoxidation process.

In order to understand the effect of Cs on the copper/oxygen system we carried out XPS measurements to examine the chemical state of the system as a function of Cs coverage. This was achieved by depositing varying amounts of Cs overlayers on a pre-oxidised Cu_2O-like surface and monitoring the changes observed in the O(1s) emission. The Cu_2O-like surface was prepared by exposing the sample to 10^5 L O_2 at 670 K [14]. Figure 3 shows the resulting curve-fitted O(1s) spectra for different Cs loadings. The Cu_2O-like surface exhibits a single peak at 529.7 eV. When Cs is added to this surface, two new

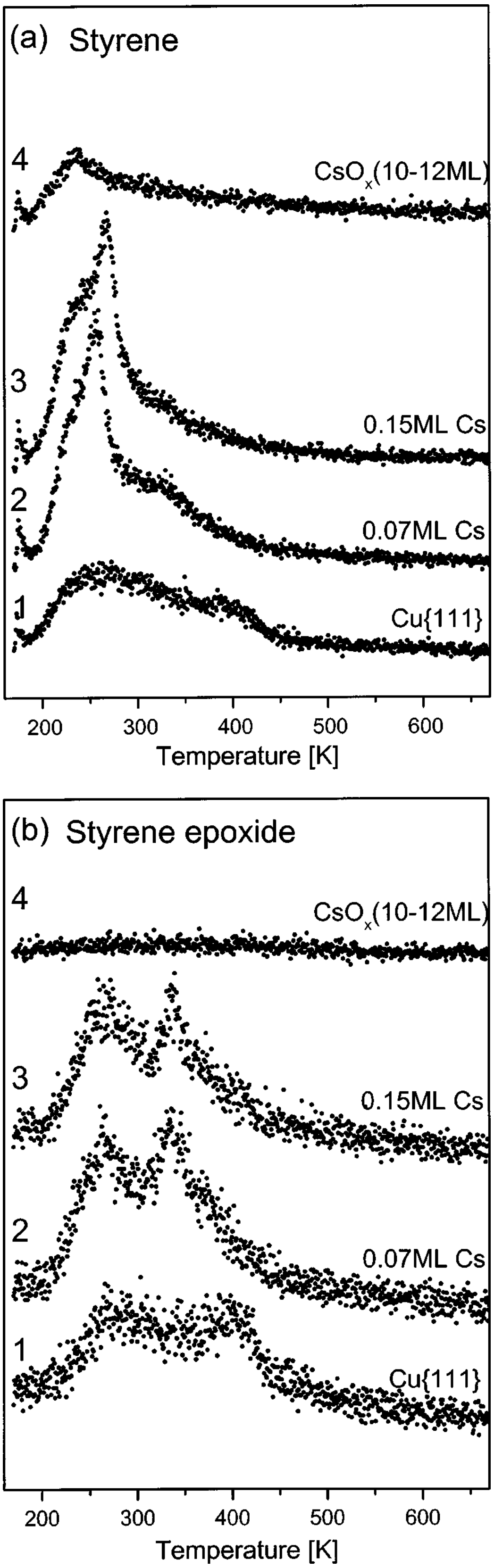

Figure 2. TPR spectra for (a) styrene ($m/z = 104$) and (b) styrene epoxide ($m/z = 91$) from (1) 0.03 ML oxygen on Cu{111}, from Cs pre-covered Cu{111} surface with Cs coverages of (2) 0.07 and (3) 0.15 ML and (4) from Cs_xO(10–12 ML)/Cu{111} surface. In the cases of 2 and 3 surfaces were exposed to a fixed oxygen dose of 0.5 L after the Cs dose.

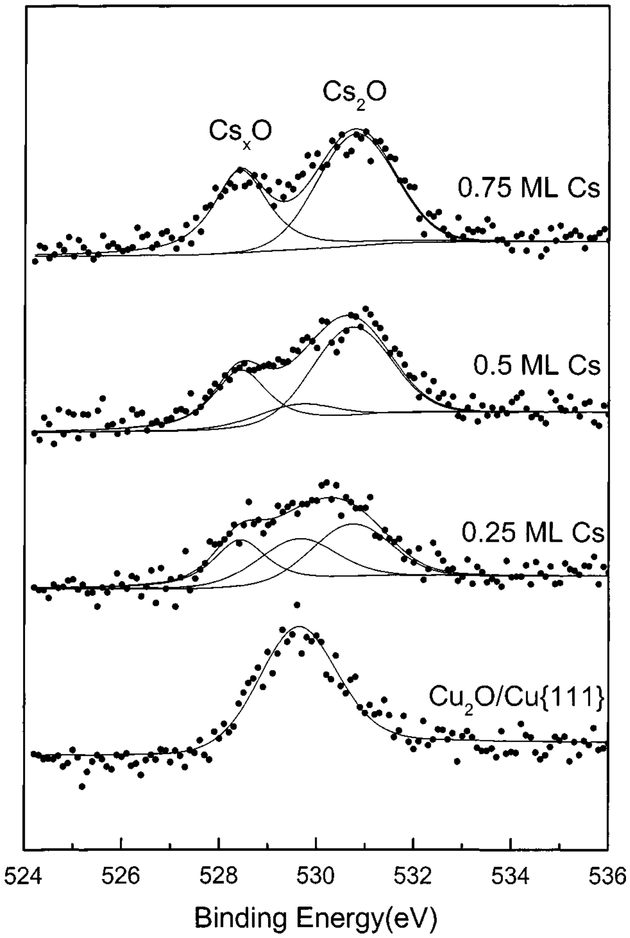

Figure 3. Changes in the O(1s) curve-fitted spectra with increasing Cs dose on the Cu_2O/Cu{111} surface at room temperature.

features appear at 528.5 and 530.8 eV, whilst the intensity of the 529.7 eV feature decreases. At a Cs coverage of 0.75 ML there is no trace of the emission centred at 529.7 eV, whilst the other two features have become more prominent. O(1s) emission at 528.5 and 530.8 eV is associated with Cs_xO suboxide and Cs_2O, respectively [17,18]. The results clearly show that Cs leads to the reduction of (catalytically inactive) oxidised copper sites to (catalytically active) metallic copper sites. Overall activity is thereby increased, with no change in selectivity. Formally we may write

$$Cu_2O + Cs \rightarrow Cu + Cs_2O + Cs_xO$$

It thus appears that at high oxygen coverages, under our conditions, Cs acts by preventing the formation of large amounts of catalytically inert copper oxide. That is, Cs promotes activity *via* the primary chemistry. This effect of Cs is to be compared with its behaviour on Ag{111}, where it acts principally to promote selectivity in the secondary chemistry, favouring desorption of the epoxide over combustion [9]. Under continuous operation this process would of course become ineffective. Its principal significance for present purposes is that it serves to confirm the important inference drawn above on the basis of the Cs-free experiments, namely that over-oxidation of the Cu surface renders it catalytically ineffective.

4. Conclusions

(1) The minimum necessary and sufficient condition for styrene epoxidation on Cu$\{111\}$ are oxygen adatoms and styrene molecules adsorbed at Cu metal sites. In this respect, Cu resembles Ag.

(2) The catalytic reaction occurs with much higher selectivity (no detectable CO_2 production) *and* at lower temperatures than it does on Ag. Cu is therefore a potentially good catalyst for alkene epoxidation.

(3) The behaviour of the $\{111\}$ surface is significantly different from that of the $\{110\}$ surface indicating that particle size effects are likely to be significant for dispersed Cu epoxidation catalysts.

(4) Styrene does adsorb on the oxidised surface, though more weakly than on clean Cu$\{111\}$. This system is catalytically inert.

(5) Submonolayer quantities of Cs enhance styrene uptake and increase the yield of styrene oxide without affecting the selectivity. This results from a “clean-off” reaction by which Cs prevents over-oxidation and hence passivation of the catalyst surface. In this respect Cu differs from Ag.

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